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CATIONIC POLYMERIZATIONS OF 136-TRIOXOCANE AND
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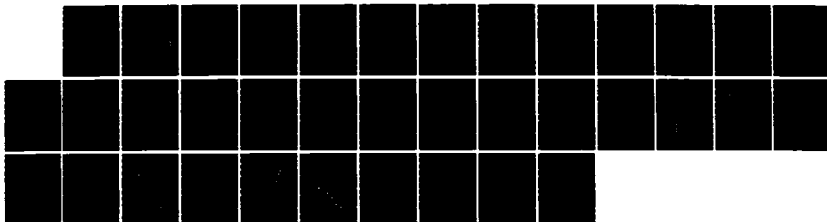
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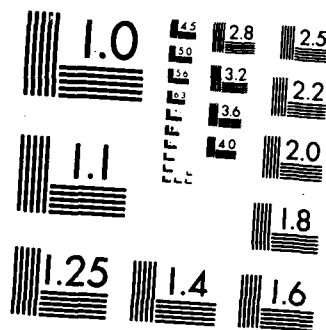
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Cationic Polymerizations of 1,3,6-Trioxocane and
2-Butyl-1,3,6-Trioxocane

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Cationic Polymerizations of 1,3,6-Trioxocane and
2-Butyl-1,3,6-Trioxocane

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ABSTRACT

$M_{sub}W$ $M_{sub}n$
The polymerization of 1,3,6-trioxocane (TOC) has been reinvestigated. The reaction occurs without an induction period to give high MW linear polymers. The degree of polymerization is not independent of conversion. Polymers having \bar{M}_n as high as 81,000 and $\bar{M}_w/\bar{M}_n \sim 1.4$ and with very strong mechanical strength can be obtained. These results contrast with earlier reports of long induction periods and products with $\bar{M}_n \sim 5,000$. Substituents at the 2 position greatly reduces the polymerizability of dioxolane and dioxpanes. It is therefore a significant result that 2-butyl-1,3,6-trioxocane (2-Bu-TOC) is readily polymerized and at a slightly faster rate than polymerization of TOC under identical conditions. The \bar{M}_n of poly(2-Bu-TOC) increases monotonically with conversion reaching a value of 7,700. The thermodynamic parameters for the polymerizations of both systems have been obtained. There is strong argument in favor of the open chain oxocarbenium ion as the propagating species for 2-Bu-TOC polymerization over the cyclic oxonium ion.

INTRODUCTION

In the course of our studies on acid catalyzed degradation of polyacetals we observed¹ that the 8-member ring monomer 2-butyltrioxocane (2-Bu-TOC)² is the main acidolysis product of poly(2-Bu-TOC). The results suggested that the unzipping mechanism involves a linear alkoxy-carbenium ion intermediate (I), eq. 1.

EQUATION I

According to the principle of microscopic reversibility, the same alkoxy-carbenium ion should be the propagating species in the polymerizations of 2-Bu-TOC.¹

In the polymerization of oxygen heterocyclic compounds, the oxonium structure for the propagating species is thought to be indisputable in the case of tetrahydrofuran.³ However, in the polymerization of dioxolane and other cyclic acetals, because of the strong stabilizing effect of the α -oxygen atom, alkoxy-carbenium ions are in equilibrium with cyclic oxonium ions. This is illustrated for 1,3-dioxolane (DOC).³

EQUATION 2

Both these species can add to another monomer molecule for propagation. Penczek *et al.*³ have argued that in the case of dioxolane the cyclic oxonium ion is responsible for the majority of propagation. Nevertheless, observations on the polymerizability of cyclic acetals having substituents on the 2 or 4 positions would seem to suggest that the oxonium ion is the dominant propagating species. For instance 2-Me-DOL⁴ and 4-Me-DOL⁵ were only oligomerized to \overline{DP} of 10 and 20, respectively, as compared to the polymerization of DOL to high molecular weight linear polymer together with macrocyclics.⁶ Whereas 1,3-dioxepane (DOP) is readily converted to high MW linear polymer by cationic initiators,⁶ the same process for 2-Me-DOP⁷ and 4-Me-DOP⁸ gave products with \overline{DP} of ca. 75. Additional methyl substituents reduces polymerizability further. Thus, 2,4-di-Me-DOP yielded only oligomeric, products even at high monomer concentration and 2,2-di-Me-DOP forms only a crystalline cyclic dimer.⁷ These results can be rationalized in terms of the severe steric hindrance to approach of a 2- and/or 4-substituted cyclic



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acetal monomer to a similarly substituted cyclic oxonium ion chain end.

Based on literature results the prospect of polymerizing 2-Bu-TOC is not promising. Polymerization of unsubstituted TOC⁹ in 1,2-dichloroethane using triethyloxonium tetrafluoroborate ($\text{Et}_3\text{O}^+\text{BF}_4^-$) as catalyst exhibits an induction period of 2 to 3 h. The polymer has $\overline{\text{DP}}$ of only about 30 which is independent of percent conversion. If the effect of a 2-Bu substituent on TOC is like that of the 2-Me substituent in the other cyclic acetals (vide supra), polymerizability of 2-Bu-TOC should be very low.

The central purpose of this work is to investigate the polymerization of 2-Bu-TOC and to deduce the probable mechanism of propagation. During the course of our study, polymerization of TOC was also investigated.

EXPERIMENTAL

Materials

Diethylene glycol, paraformaldehyde, boron trifluoride etherate, tetralin, and triethyloxonium tetrafluoroborate (1 M soln in MeCl_2) were from Aldrich Chemical Company. Benzene, toluene and methylene chloride were Fisher Reagent grade solvents.

Diethylene glycol and benzene were dried with Molecular Sieves and distilled prior to use. Tetralin and methylene chloride were purified by distillation over CaH_2 . Boron

trifluoride etherate was distilled immediately before use. Paraformaldehyde was used as received. Amberlite IR-120 was treated with 10% hydrochloric acid overnight, washed with water, and then with methanol. The resin was oven dried at 100°.

Monomers

1,3,6-Trioxocane was prepared by the condensation of diethylene glycol and paraformaldehyde in the presence of Amberlite IR-120 according to Astle's method.¹⁰ It was purified by distillation from LiAlH_4 and collection of the fraction with the literature, b.p. 154-155°C.

2-Butyl-1,3,6-trioxocane was prepared as described previously.¹ It was refluxed with CaH_2 , then distilled at 0.3 mmHg at 44-45°C.

The monomers were analyzed by gas chromatography showing purities in excess of 99%.

Polymerization

Polymerization was carried out in a Schlenk tube which had been flame dried under vacuum and filled with purified nitrogen. The tube was equipped with a magnetic stir bar, fitted with a rubber septum. Both the monomer solution and catalyst solution were injected by syringe. Either methylene chloride or toluene was used as solvent. The monomer solution was equilibrated at the reaction temperature in a thermostated bath prior to

introduction of catalyst. Samples were taken with a stainless steel cannula at intervals during the course of polymerization. The sample was quenched with triethylamine, precisely weighed, and a known amount of tetralin according to conversion was added as GC standard. The mixture was analyzed with GC. Conversion was calculated, using a calibration curve, from the peak area ratio for the monomer and tetralin.

Poly(TOC) was isolated by pouring the reaction mixture into cold methanol and allowing it to stand at -20° for several h. The precipitated poly(TOC) was collected by filtration while cold and dried at 120° in vacuo. The white waxy polymer has the known T_m of 36° by DSC.

It was not possible to precipitate poly(2-Bu-TOC). Instead, the polymerization mixture was washed with water several times. The organic phase was dried with anhydrous $MgSO_4$ overnight. After the solvent was removed by distillation, the residual solvent was removed from polymer at 120° in vacuo.

Equilibrium Monomer Concentration

Different polymer work-up procedures were desired for the determination of $[M]_e$ by GC which obviated any possible depolymerization occurring in the injection port. For TOC, the polymerization mixture at desired conversion was quenched, a weighed amount of tetralin was added, the mixture cooled to -196° and evacuated. With the stopcock to the vacuum pump closed, the

polymerization mixture was heated to 120° while a receiver section was maintained at -196° to effect cryogenic distillation of unconsumed monomer. In the case of polymerization of 2-Bu-TOC, the mixture was first diluted with solvent to about four times volume, followed by GC analysis. For the determination of $[M]_0$ we used 1,2-dichloroethane as the solvent. This choice is necessitated by the fact that CH_2Cl_2 is too volatile, whereas toluene is a poor solvent for the polymer and the polymerization mixture became a gel rendering cryogenic distillation inefficient.

Analytical Methods

Gas chromatography was carried out on a Hewlett-Packard 5790A chromatograph using a Foxboro Super Pak II 6 ft x 1/8 in o.d. column, temperature programmed (30° for 3 min, 30° to 200° at 20°/min, 200° for 5 min for analyzing 2-Bu-TOC; 30° for 3 min, 30° to 120° for 10°/min, 120° for 5 min for analyzing TOC.

1H -NMR spectra were obtained using Perkin-Elmer R-12 and Varian Associates XL-300 instruments. $CDCl_3$ was used as the solvent, and tetramethylsilane (TMS) was used as internal standard. In the case of low temperature 1H -NMR, $CDCl_3$ and TMS were sealed in the capillary which was put into the NMR tube with the sample.

GPC was carried out on a Waters Associates GPC instrument. Tetrahydrofuran was used as solvent, (flow rate 0.8 mL/min), 10^5

A and 10^3 A columns were used. Number average molecular weight \bar{M}_n , weight average molecular weight \bar{M}_w and polydispersity D were calculated from the standard curve determined using monodispersity polystyrene samples.

DSC curves were obtained from Perkin-Elmer DSC-IV. The temperature was calibrated using indium and cyclohexane.

RESULTS AND DISCUSSION

The polymerizations of trioxocanes were performed with two different catalysts and solvents. Polymerizations initiated by triethyl oxonium tetrafluoroborate ($\text{Et}_3\text{O}^+\text{BF}_4^-$) in methylene chloride at -10° have very fast rates reaching equilibrium monomer conc., $[\text{M}]_e$, within 15 min (Figure 1). It is worthy of note that the polymerizations commenced immediately upon mixing of monomer and catalyst. This is contrary to the long induction periods observed by Okata and coworkers for TOC⁹ and 1,3-dioxolane in 1,2-dichloroethane initiated by $\text{Et}_3\text{O}^+\text{BF}_4^-$.¹¹ It seems that an inhibitor must have been presented in their system.

The rates of polymerization of TOC and 2-Bu-TOC in CH_2Cl_2 are too rapid to be monitored with accuracy. Since ionic polymerizations have reduced rates in nonpolar media, the kinetics were studied at -10° using toluene as the solvent. It can be seen in Figure 2 that 2-Bu-TOC actually approached $[\text{M}]_e$ faster than TOC. This result is contrary to expectations based on behavior of other 2- and/or 4- substituted cyclic acetals

discussed above.

Polymerization of TOC

The rate constant of propagation in the case of polymerization without an induction period can be obtained by the relationship

$$\log\left(\frac{[M]_t - [M]_e}{[M]_0 - [M]_e}\right) = k_p[C^*]_0 t / 2.303 \quad (3)$$

where $[M]_0$ and $[M]_t$ are the monomer concentrations at time zero and t , respectively, and $[C^*]_0$ is the concentration of propagating species. However, the latter value is not known. The one may use the slope of the first order plots (Figure 3) to calculate $k'_p[C]_0$ where k'_p is the apparent rate constant and $[C]_0$ is the initiator concentration. If the polymerizations of TOC and DOL are to be living cationic, eq. 3 is valid and the values of k_p are $(2.4 \pm 0.4) \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ and $(3.4 \pm 0.7) \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$, respectively for TOC and 2-Bu-TOC at -10° .

In polymerization of cyclic acetals sometimes both linear and macrocyclic polymers are produced. Okata et al.⁹ reported \bar{M}_n values of up to $\sim 3,000$ only for their $\bar{\text{poly}}(\text{TOC})$ using vapor phase osmometry. In our work the MW of a $\bar{\text{poly}}(\text{TOC})$ is much greater than this. Furthermore, the GPC curves (Figure 4) showed the formation of both linear and macrocyclic polymers. The

fraction eluted with smallest retention volume is assumed to be that of linear high MW poly(TOC). There is one small and one large peak (designated by m) at higher retention volumes which are probably the macrocyclics. Finally, there is a solvent peak(s) the intensity of which is very dependent on the particular sample and unknown variation on how the sample was injected into the GPC.

If one calculates MW and MWD (molecular weight distribution = P.D. polydispersity = \bar{M}_w/\bar{M}_n) including the entire trimodal distribution curve, the results are without much quantitative significance. Since the high MW linear fraction is by far the dominant one, we have resolved the trimodal GPC curves into three Gaussian components and report the MW values for the major GPC peak in Table I. It took several h of polymerization for the MW to reach the maximum constant values of $\bar{M}_n = (2.70 \pm 0.04) \times 10^4$ and $\bar{M}_w = (3.86 \pm 0.05) \times 10^4$. The MWD is quite narrow having a constant P.D. value after 7 h of polymerization of 1.43 ± 0.04 . The polymerization has partially living cationic characteristics. These results are contrasted with those of Okada et al.⁹ who found after ca. 3 h of induction period $\bar{M}_n \sim 3000$ which is the same at all conversion. The same unknown inhibitors which cause the induction period may also be limiting the chain growth.

In fact the polymerizations described in Table I were probably complicated by the sampling process. We have polymerized TOC at 0° ([TOC] = 2.5 M in toluene; [BF₃·Et₂O] = 25

Table I
Molecular Weights of Poly(TOC)

No.	6-3	6-5	6-6	6-7	6-8	K-6
Reaction time, ^a hr	3	7	9	11.5	12.5	30.5
Conversion, %	40.7	74.0	84.3	87.9	91.1	94.0
\bar{M}_n	15300	27400	27300	26500	26700	27000
\bar{M}_w	23400	38000	38200	39300	39000	38500
P.D.	1.53	1.38	1.40	1.48	1.46	1.43

^aPolymerizations at -10° for [TOC]₀ = 2.67 M in toluene initiated by 26.7 mM BF₃·Et₂O.

Table II
Molecular Weights of Poly(2-Bu-TOC)

No.	5-3	5-5	5-7	5-10	5-13	K-5
Reaction time, ^a hr	2	4	6	9	12	24
Conversion, %	56.3	77.9	84.2	86.7	90.4	91.2
\bar{M}_n	3450	5150	6330	6290	6780	7710
\bar{M}_w	5500	8210	9970	10000	10600	12200
P.D.	1.60	1.59	1.57	1.59	1.57	1.58

^aPolymerization at -10° for [2-Bu-TOC]₀ = 2.56 M in toluene initiated by 25.6 mM of BF₃·Et₂O.

mM) for 20 h without taking samples from it. The poly[TOC] isolated exhibits only one narrow GPC peak (Figure 5). The MW values are: $\bar{M}_n = 8.1 \times 10^4$, $\bar{M}_w = 1.15 \times 10^5$ and $\bar{M}_w/\bar{M}_n = 1.43$. This poly(TOC) is flexible, very tough and appears opaque and slightly yellow. Therefore, poly(TOC) with interesting and useful mechanical and physical properties can be obtained.

The $[M]_e$ was determined by GC on the volatile components in the absence of polymer as described above. Results at various temperatures are plotted in Figure 6. Using Dainton's equation,¹²

$$\ln[M]_e = \frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R} \quad (4)$$

with $\Delta G^\circ_{eq} = 0$ for a 1 M solution in monomer. We obtained $\Delta H^\circ_{ss} = -3.1 \text{ kcal mole}^{-1}$, $\Delta S^\circ_{ss} = 5.1 \text{ cal (mole K)}^{-1}$ and $T_c = 330^\circ$. However, the actual value of T_c for poly(TOC) may be even higher because in the 0° polymerization without sampling (*vide supra*), the conversion is more complete to give 81,000 \bar{M}_n polymer. In this case, it was not possible to determine the value of $[M]_e$ by the GC method because the reaction mixture is a gel-like mass of swollen polymer.

Polymerization of 2-Bu-TOC

Polymerization of 2-Bu-TOC was carried out under the same

conditions described above for TOC. The results are summarized in Table II. The GPC curves of the poly(2-Bu-TOC) (Figure 7) showed similar trimodal distribution with a solvent peak as seen with poly(TOC). Therefore, linear and macrocyclic polymers were obtained in both cases. The \bar{M}_n values increase monotonically with conversion (Figure 8). That the line does not intersect the origin can be readily understood if there is some loss of very low MW products at low conversion.

We have also performed 2-Bu-TOC polymerization without sampling. Unlike in the case of TOC, the products have the same \bar{M}_n and P.D. as those polymers isolated from extracted samples at the same conversion.

The slow, monotonic increase of molecular weight throughout the course of polymerization can be understood as a consequence of the ability of living oxocarbenium ion chain ends to equilibrate with unreactive vinyl ether chain ends by loss of β -protons,

EQUATION 5

Vinyl ether chain ends can be reactivated by protonation (reverse

of eq. 5). This pathway is unavailable to polymerizing TOC itself, hence poly(TOC) attains much higher molecular weights under identical conditions. Alternatively, the proton could initiate another chain.

Variation of $[2\text{-Bu-TOC}]_e$ with temperature is plotted in Figure 9. From the slope and intercept we found $\Delta H^\circ_{ss} = -1.2$, $\Delta S^\circ_{ss} = +3.7 \text{ cal (mole K)}^{-1}$, and $T_c = 40^\circ$. Experimental errors may be large owing to difficulties in separation of low MW polymer from unreacted monomer and related experimental difficulties which were not encountered in the case of poly(TOC).

Copolymerization of TOC and 2-Bu-TOC

Copolymerizations of TOC and 2-Bu-TOC were conducted at -10° in 1,2-dichloroethane for 24 h. The amount of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was 1% of the total number of moles of the comonomers. Products were isolated by the procedure used for poly(2-Bu-TOC). GPC curves showed a single high MW peak (Figure 10); mixtures of homopolymers would give different GPC results. The MW's of the copolymers are given in Table III. A range of comonomer peak compositions were studied. The copolymer compositions were analyzed by NMR. The results in Table III show the copolymerization to be nearly ideal.

Thermodynamics

Owing to relief of ring strain, polymerization of most small

Table III
Copolymerizations of TOC and 2-Bu-TOC^a

[2-Bu-TOC] in feed, mole %	47.0	56.5	71.8
[2-Bu-TOC] in copolymer, mole %	49.4	57.2	71.1
\bar{M}_n	3,110	2,910	2,540
\bar{M}_w/\bar{M}_n	2.1	2.2	2.2

^aCopolymerization in 1,2-dichloroethane at -10° initiated by 1 mole % of $\text{BF}_3 \cdot \text{Et}_2\text{O}$.

medium ring heterocycles is exothermic. Ring strain of the 8-membered cyclic 1,3-formal¹³ is $\Delta H^\circ_{ss} = -3.94 \text{ kcal mole}^{-1}$ which lies between the values of -5.1 and -3.5 kcal mole^{-1} for the 5- and 7-membered analogs,^{14,15} respectively. Any substituent tends to increase non-bonded repulsions in the polymer resulting in lower exothermicity for the polymerization. For multiply substituted cyclic acetals, the free energy change becomes positive and there is no polymerization (*vide supra*). The thermodynamic properties of some cyclic acetals are compared in Table IV.

Methyl substitution at the 4 position in DOL or DOP decrease $-\Delta H^\circ_{ss}$ by 1.0 and 1.4 kcal mole^{-1} , respectively. Substitution causes only small changes in ΔS°_{ss} for these compounds. The

Table IV
Thermodynamic Parameters of Polymerization of Cyclic Acetals

Monomer	Solvent	$-\Delta H_{ss}^{\circ}$ kcal mol ⁻¹	$-\Delta S_{ss}^{\circ}$ cal (mole K) ⁻¹	$T_c,$ °C	Ref.
TOC	1,2-dichloroethane	3.1±0.1	5.1±0.3	330	This work
2-Bu-TOC	1,2-dichloroethane	1.9±0.2	3.9±0.5	220	This work
DOP	methylene chloride	3.6	11.5	27	7,8
2-Me-DOP	methylene chloride	2.1	8.9	-37	7,8
4-Me-DOP	methylene chloride	2.2	9.3	-33	7,8
DOL	methylene chloride	4.2	11.4	95	16
4-Me-DOL	methylene chloride	3.2	12.7	-21	16

ΔH_{ss}° for 2-Me-DOP is 1.5 kcal mole⁻¹ smaller than for DOP. The degree of polymerization of 2-Me-DOL is too low⁴ for the determination of thermodynamic parameters. Butyl substitution at C₂ in TOC causes a 1.9 kcal mol⁻¹ decrease in $-\Delta H_{ss}^{\circ}$, comparable to the increments cited above.

Mechanism

The ¹H NMR spectrum of poly(2-Bu-TOC)¹ is consistent with a regular head-to-tail structure. The polymers prepared by condensation of diethylene glycol with pentanal and by polymerization of 2-Bu-TOC exhibit identical spectra. This

arises from preferential ring opening at the more reactive acetal C-O bonds, the higher basicity of the 6-oxygen notwithstanding. The ambiguity of the propagating species in cyclic acetal polymerization has been discussed above. The nearly identical polymerization rates we have observed for TOC and 2-Bu-TOC in toluene are consistent only with an oxocarbenium ion propagating species in the case of 2-Bu-TOC. If the propagation step involved attack of 2-Bu-TOC monomer on a cyclic oxonium ion chain end, eq. 7, steric hindrance involving butyl-butyl interactions should slow propagation drastically.

EQUATION 6

2-Bu-TOC is able to avoid this by formation of the open-chain oxocarbenium ion (I_2 in eq. 1) and subsequent propagation by nucleophilic attack of I_2 by 2-Bu-TOC. Formation of a secondary oxocarbenium ion in this case is far more favorable than formation of its primary counterpart in the case of TOC owing to the much greater stability of the secondary carbenium ion.

Our data do not permit identification of the propagating species in the case of TOC. However, the nearly identical

polymerization rates for TOC and 2-Bu-TOC are most easily understood in terms of different propagation mechanisms. If both proceeded via oxocarbenium ions, the much lower stability of the primary ion from TOC should result in a much lower relative rate of polymerization for TOC. We suggest that the extra steric hindrance in attack of the secondary oxocarbenium ion, I would be insufficient to compensate for the lower rate of formation of the less stable primary ion from TOC chain ends.

A plausible reason for the lower molecular weight of poly(2-Bu-TOC) has been presented above.

Conclusion

The polymerization of TOC is more facile than earlier reported.⁹ Not only is there no induction period the MW of poly(TOC) is not independent of conversion. In fact very high MW ($\bar{M}_n = 81,000$) of very strong mechanical properties can be obtained under certain conditions. Rather unexpected results of this work is the polymerizability of 2-Bu-TOC. The MW of poly(2-Bu-TOC) reached 7,700.

Acknowledgement

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CAPTIONS FOR FIGURES

- Fig. 1. Polymerization time-conversion curves using 1 mole of Et_3OBF_4 as catalyst, Me_2Cl_2 as solvent at temp = -10° ; (O) 1,3,6-trioxocane $[\text{M}]_0 = 2.56 \text{ M}$; (O) 2-butyl-1,3,6-trioxocane, $[\text{M}]_0 = 2.53 \text{ M}$.
- Fig. 2. Polymerization time-conversion curves using 1 mole % $\text{BF}_3\text{Et}_2\text{O}$ as catalyst, toluene solvent at temp = -10° : (O) 1,3,6-trioxocane $[\text{M}]_0 = 2.67 \text{ M}$; (O) 2-butyl-1,3,6-trioxocane, $[\text{M}]_0 = 2.56 \text{ M}$.
- Fig. 3. First order plots of data in Figure 2.
- Fig. 4. GPC curves of samples obtained during the polymerization of 1,3,6-trioxocane at 74.0, 84.3, 87.9 and 91.1% conversion.
- Fig. 5. GPC curve of poly(1,3,6-trioxocane) obtained in a continuous run, see text for discussion.
- Fig. 6. Relationship between $\ln[\text{M}]_0$ and $1/T$ for TOC.
- Fig. 7. GPC curves of samples obtained during the polymerization of 2-butyl-1,3,6-trioxocane at 56.3, 77.9, 84.2, 86.7, 90.4% conversion.

Fig. 8. Variation number average molecular weight with conversion during the polymerization of 2-butyl-1,3,6-trioxocane. Conditions $[M]_0$ are as in Figure 2.

Fig. 9. Plot of $\ln[M]_e$ versus T^{-1} for 2-butyl-1,3,6-trioxocane.

Fig. 10. GPC curves of copolymers of 1,3,6-trioxocane and 2-butyl-1,3,6-trioxocane, 2-butyl-1,3,6-trioxocane mole % in copolymers: 49.4, 57.2, 71.7%.

Fig. 11. 300 MHz ^1H NMR spectrum of the mixture of 2-butyl-1,3,6-trioxocane and $\text{BF}_3\text{Et}_2\text{O}$ in toluene. Internal standard: tetramethylsilane temp -40° .

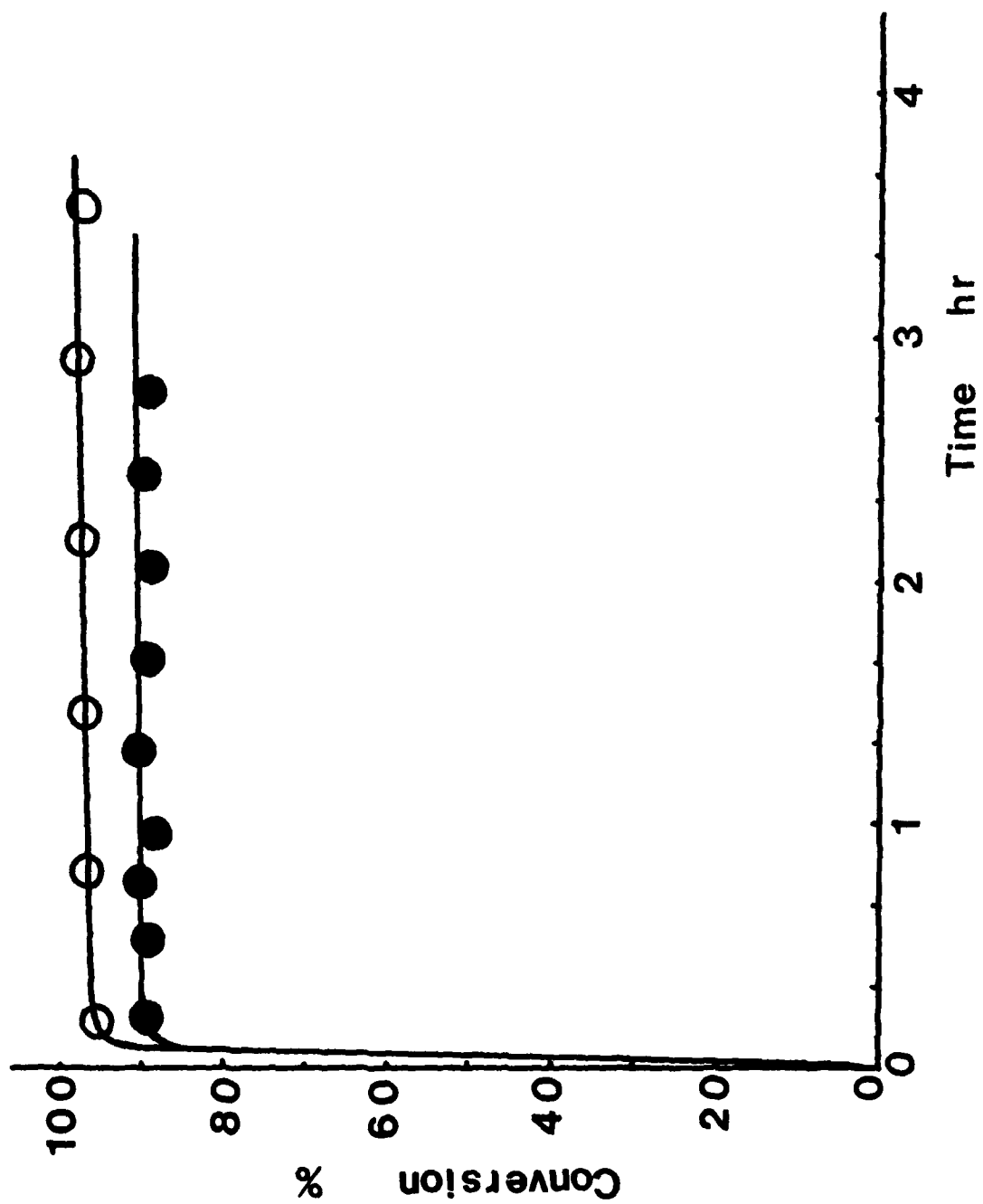
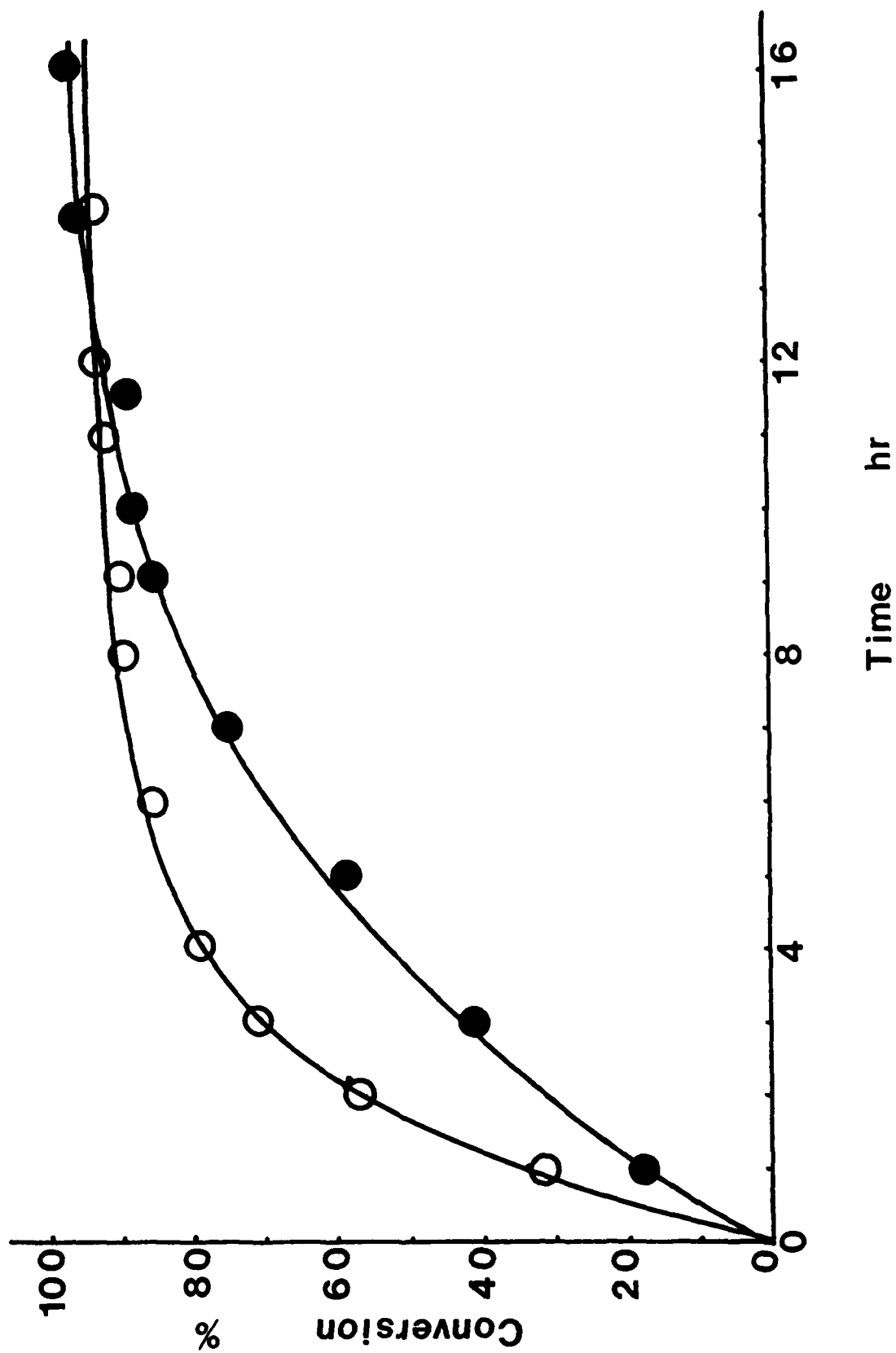


Fig. 2



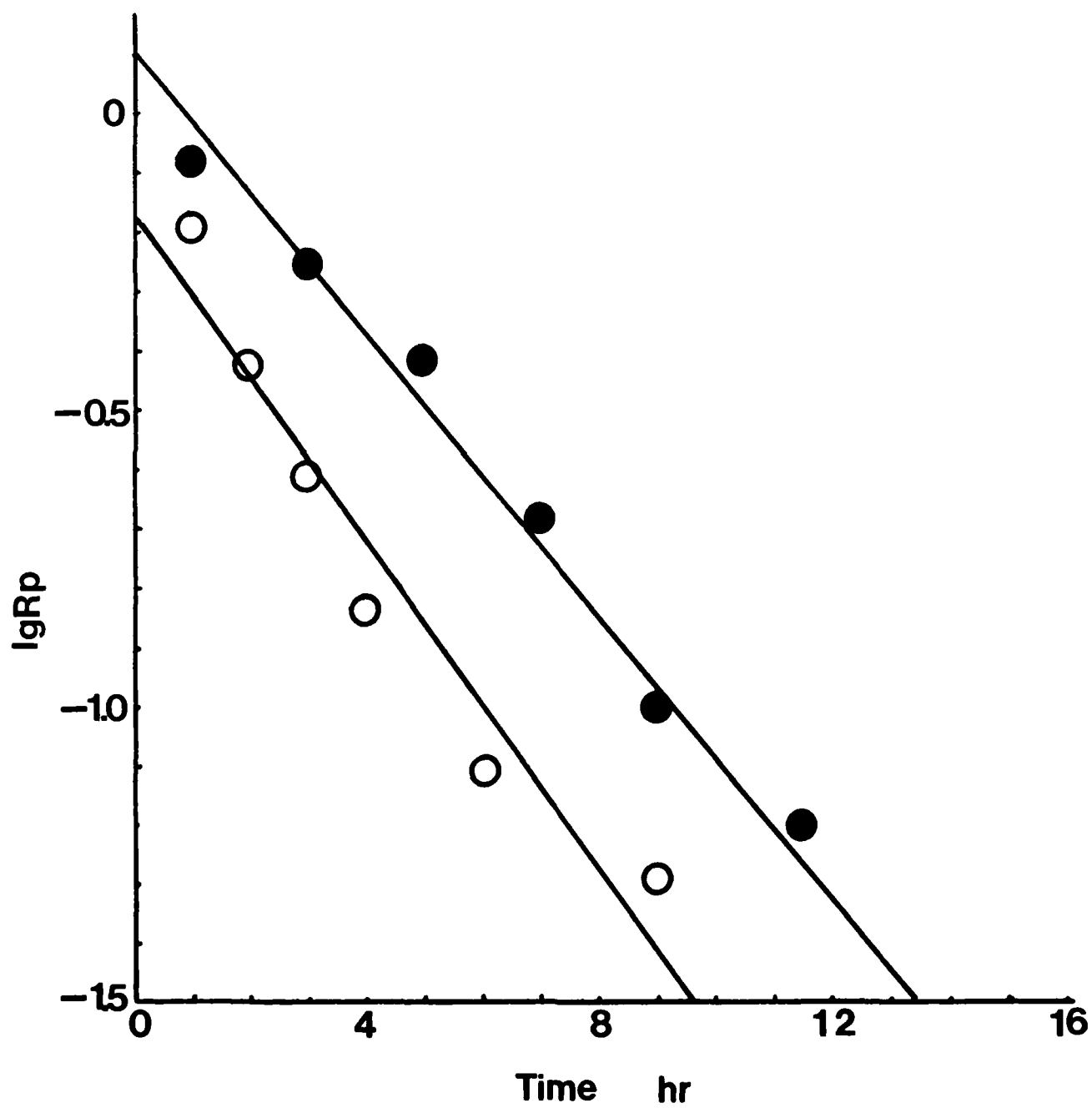


Fig 4

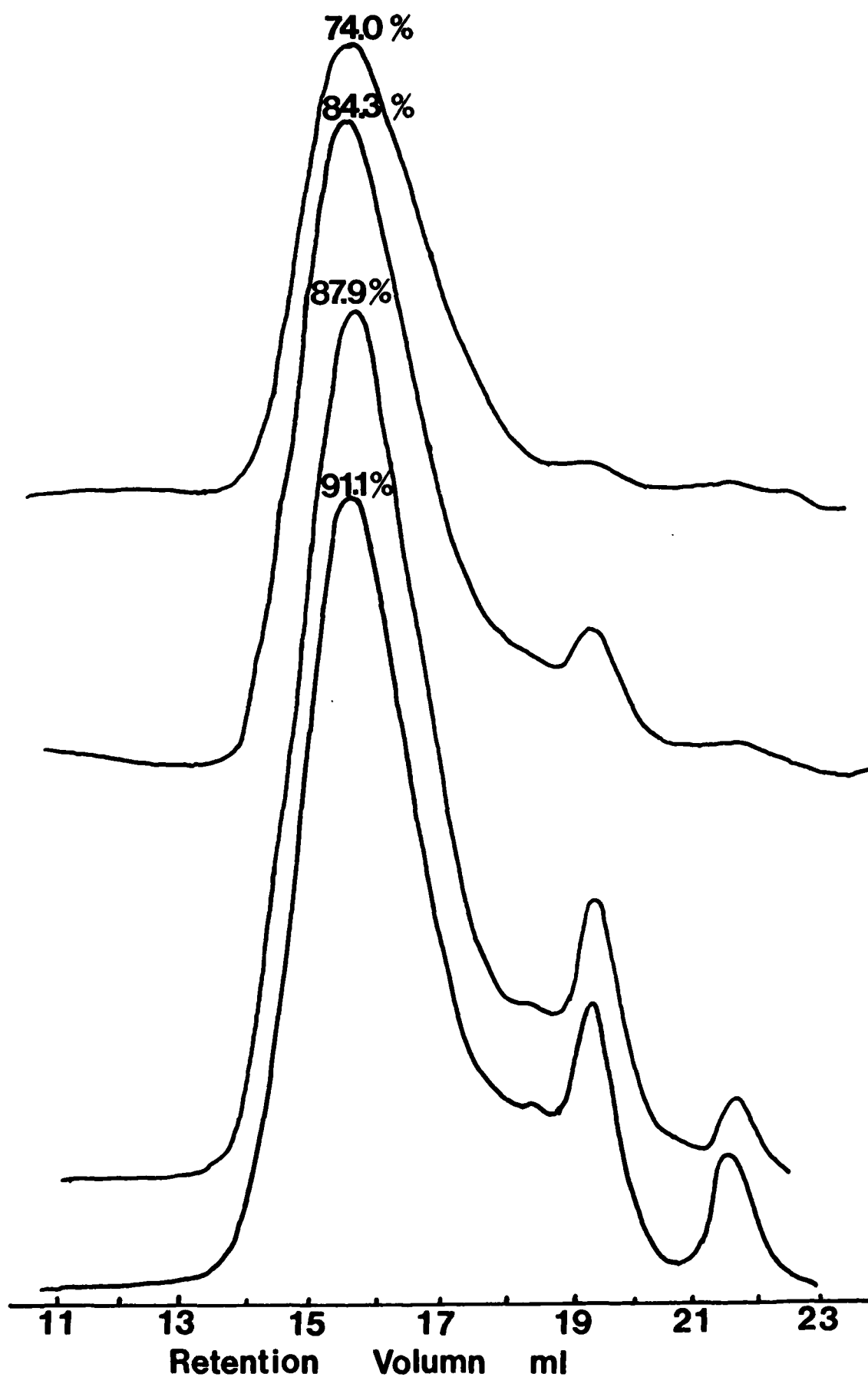
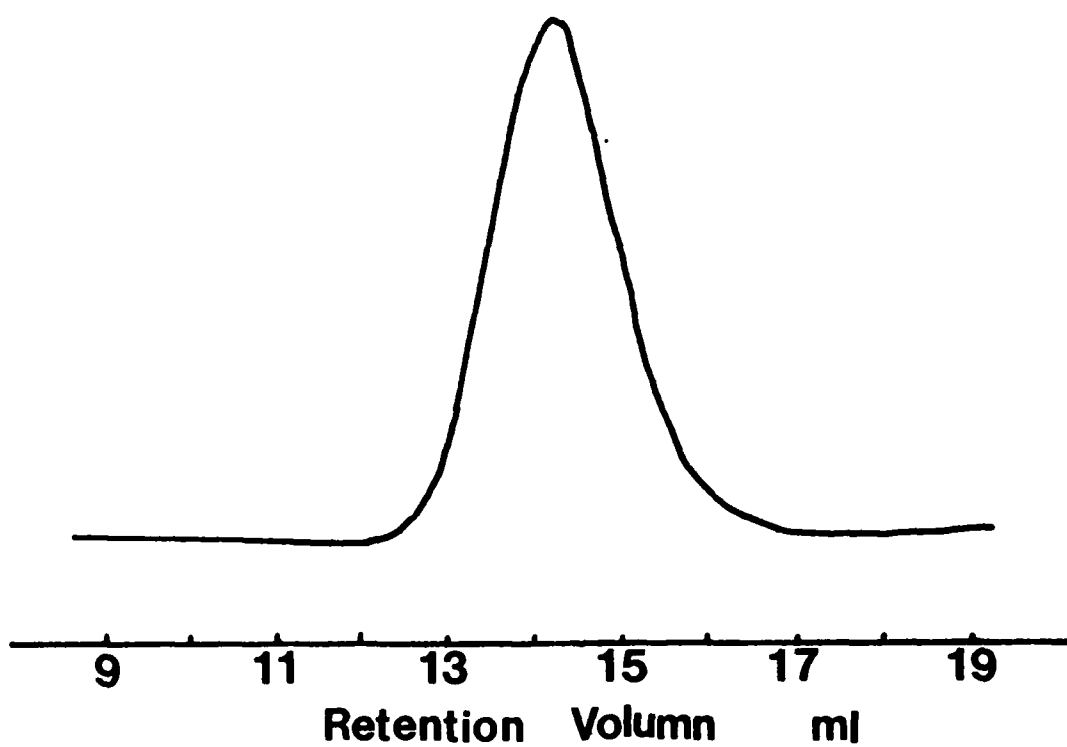
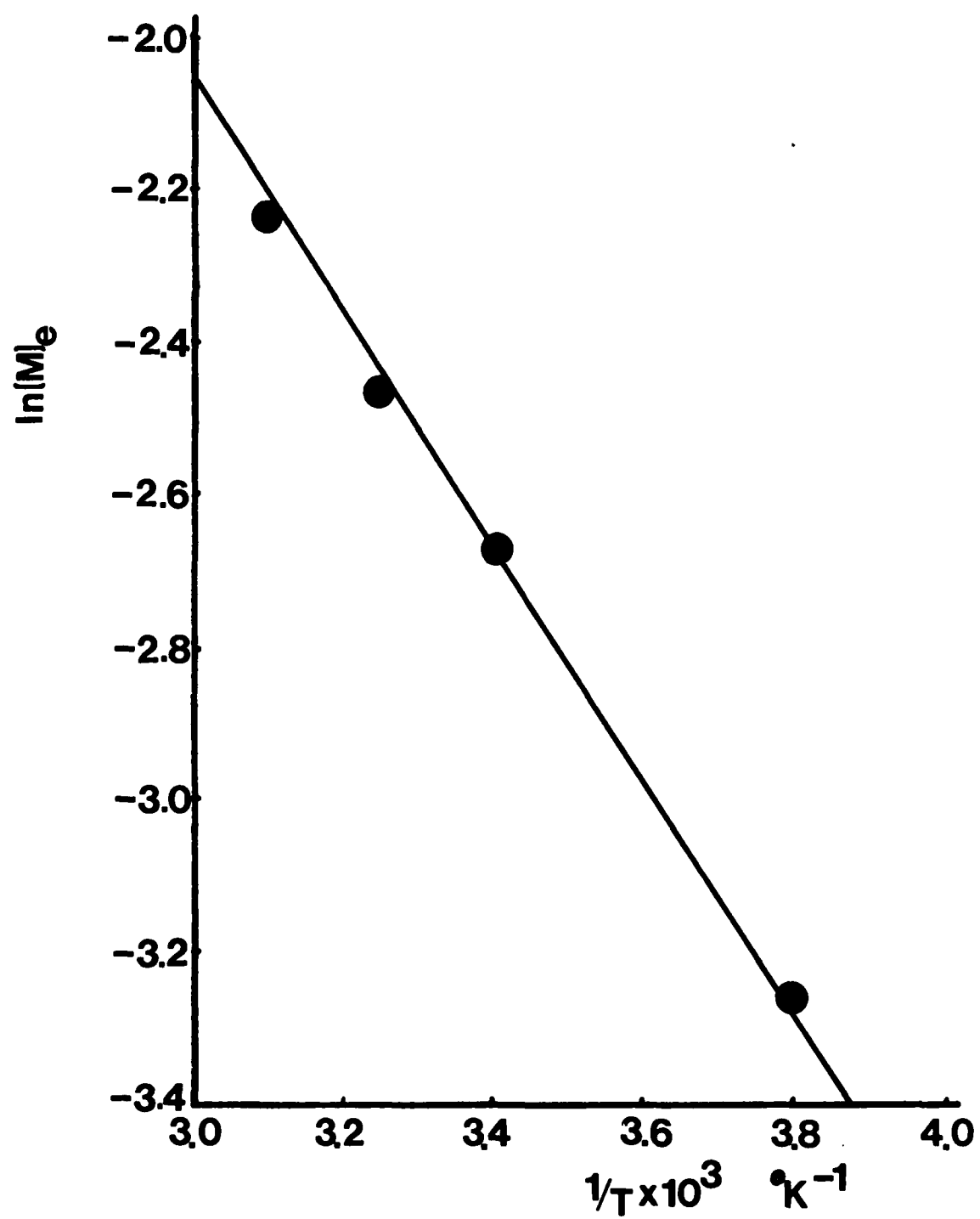
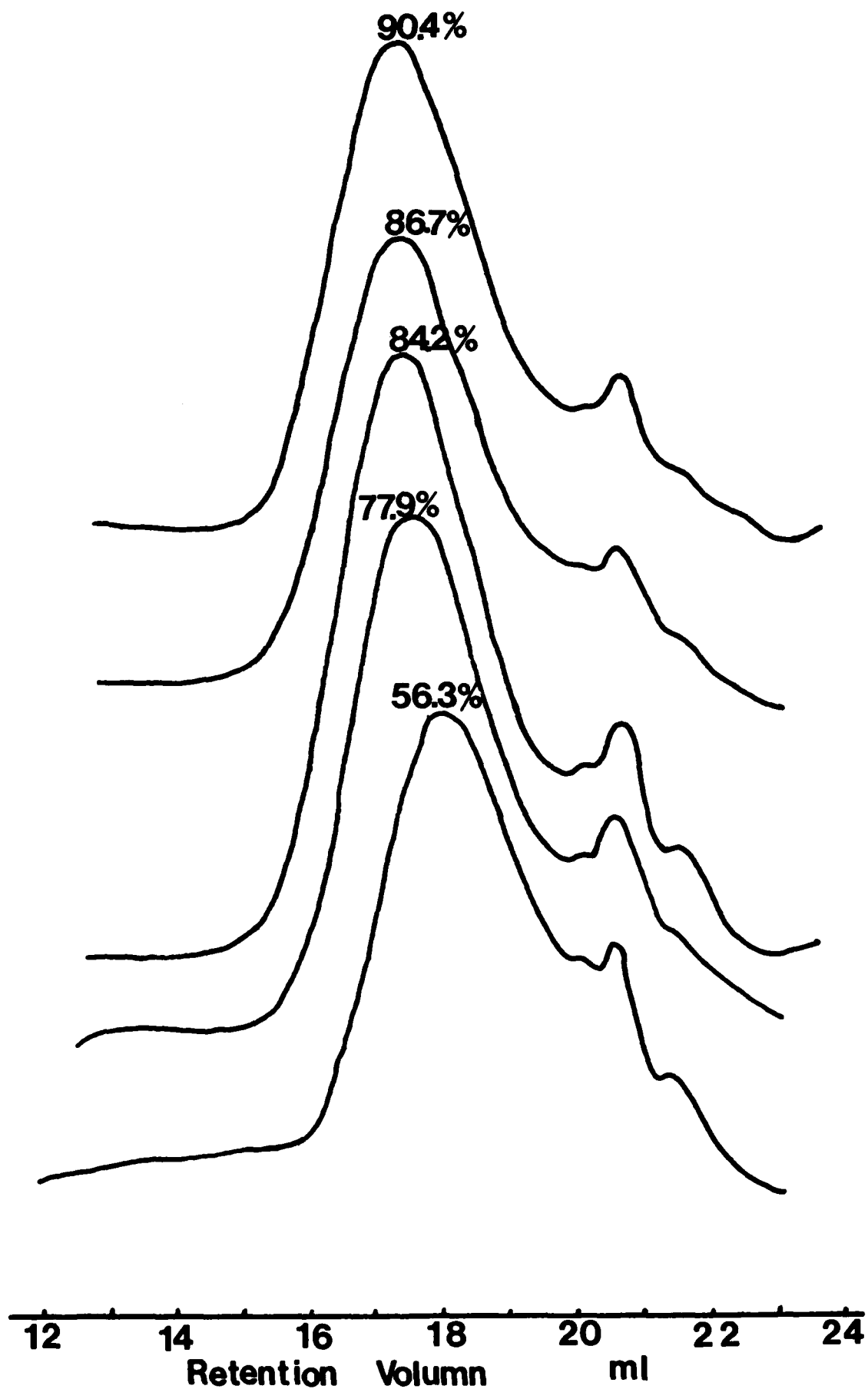
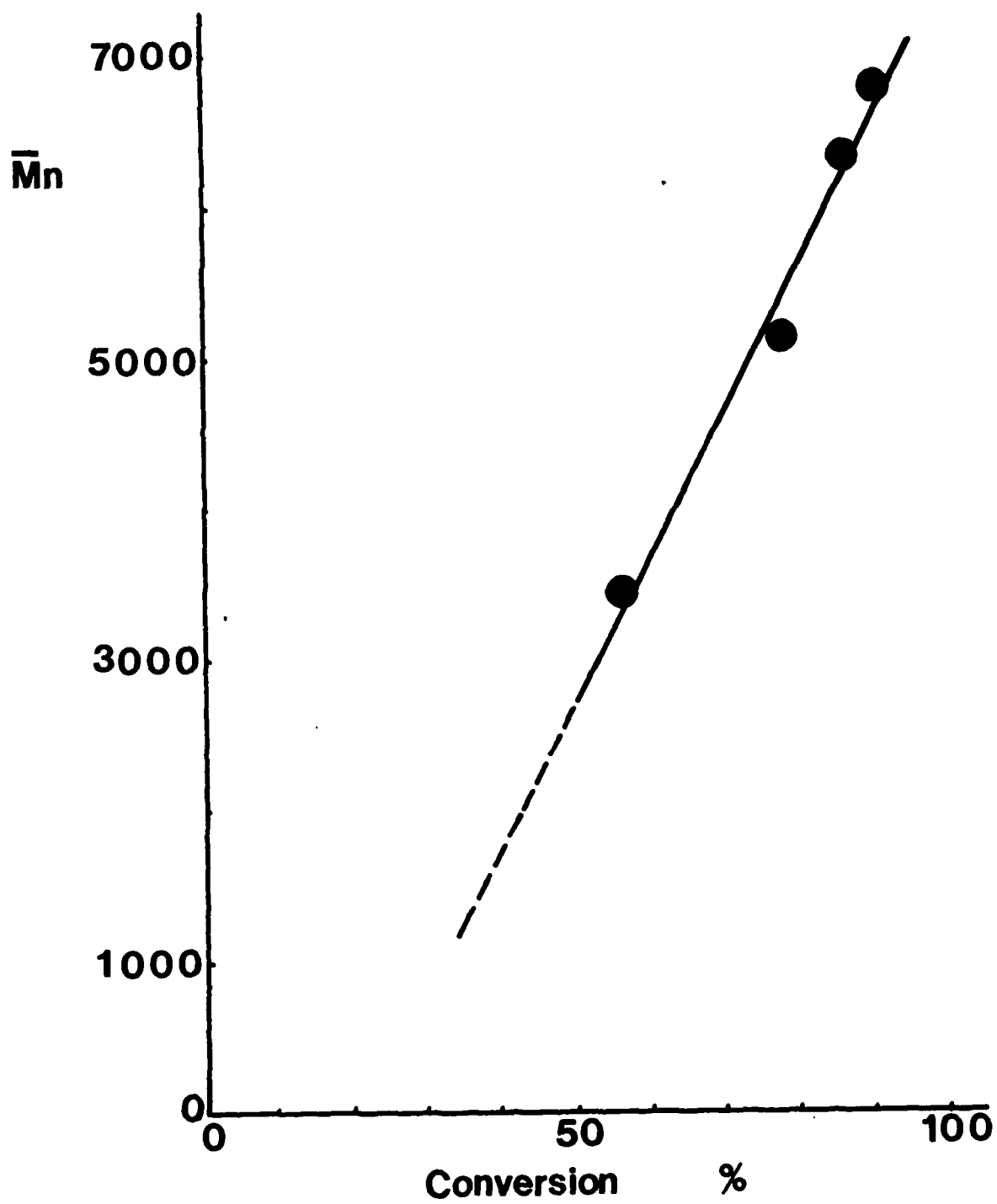


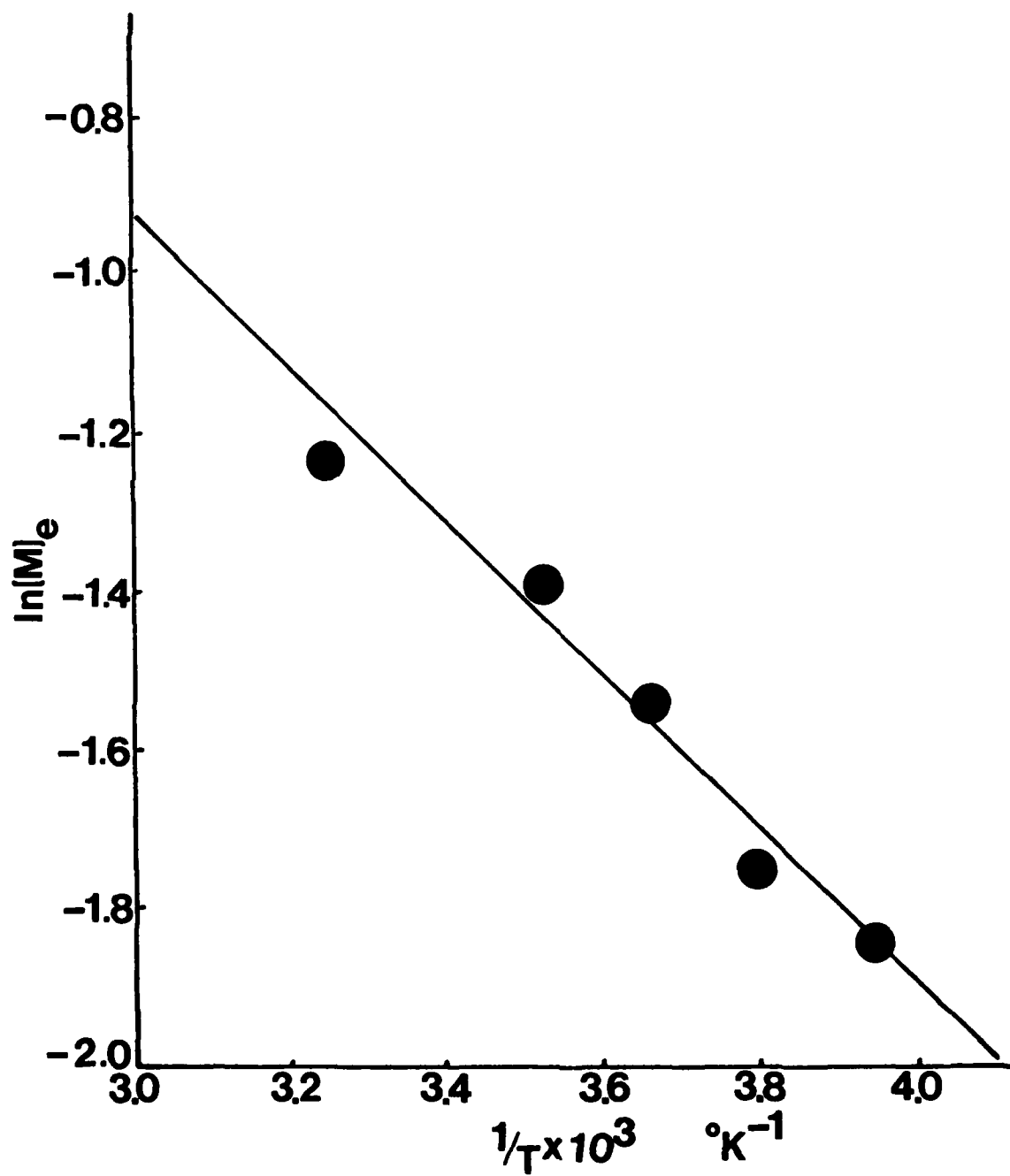
Fig 5

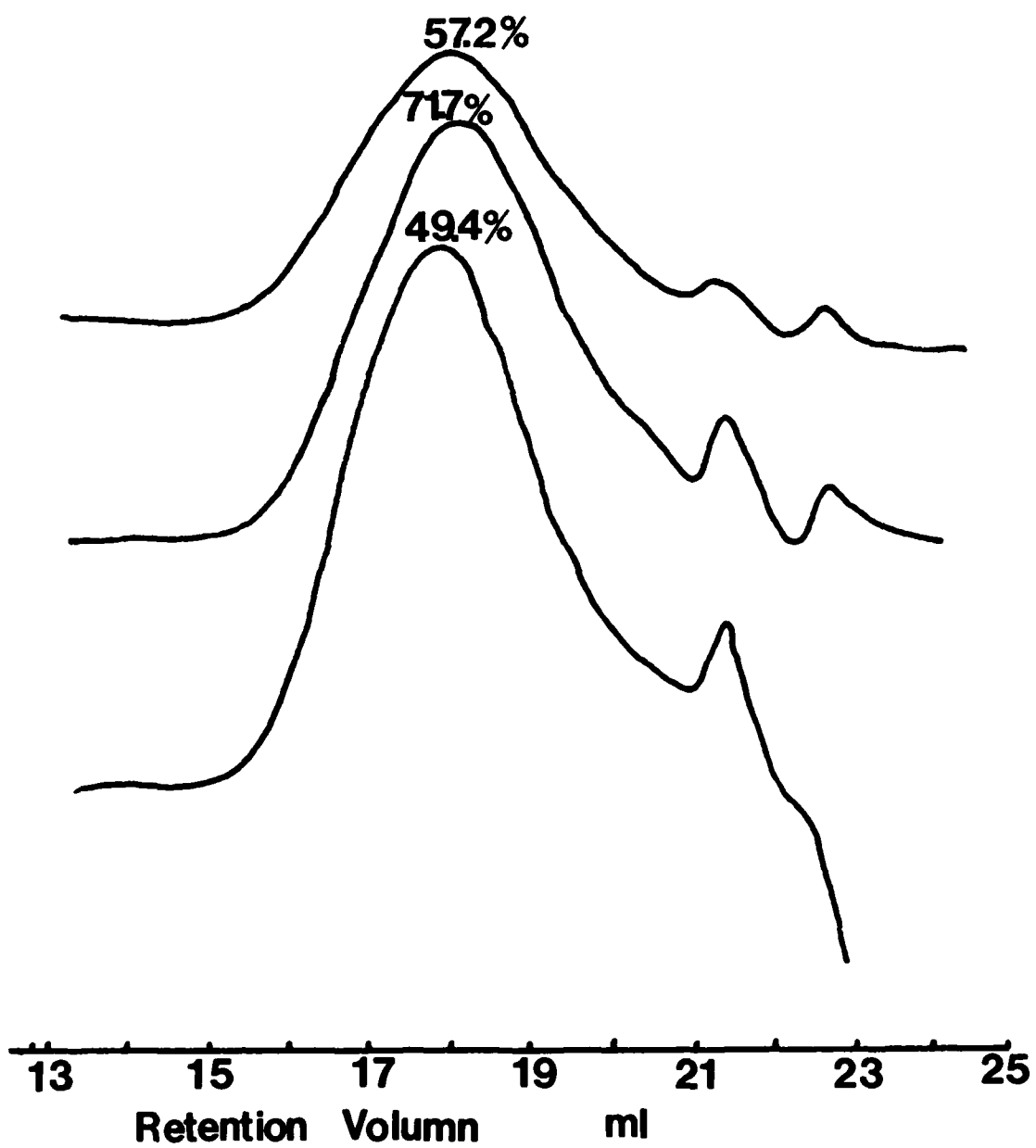


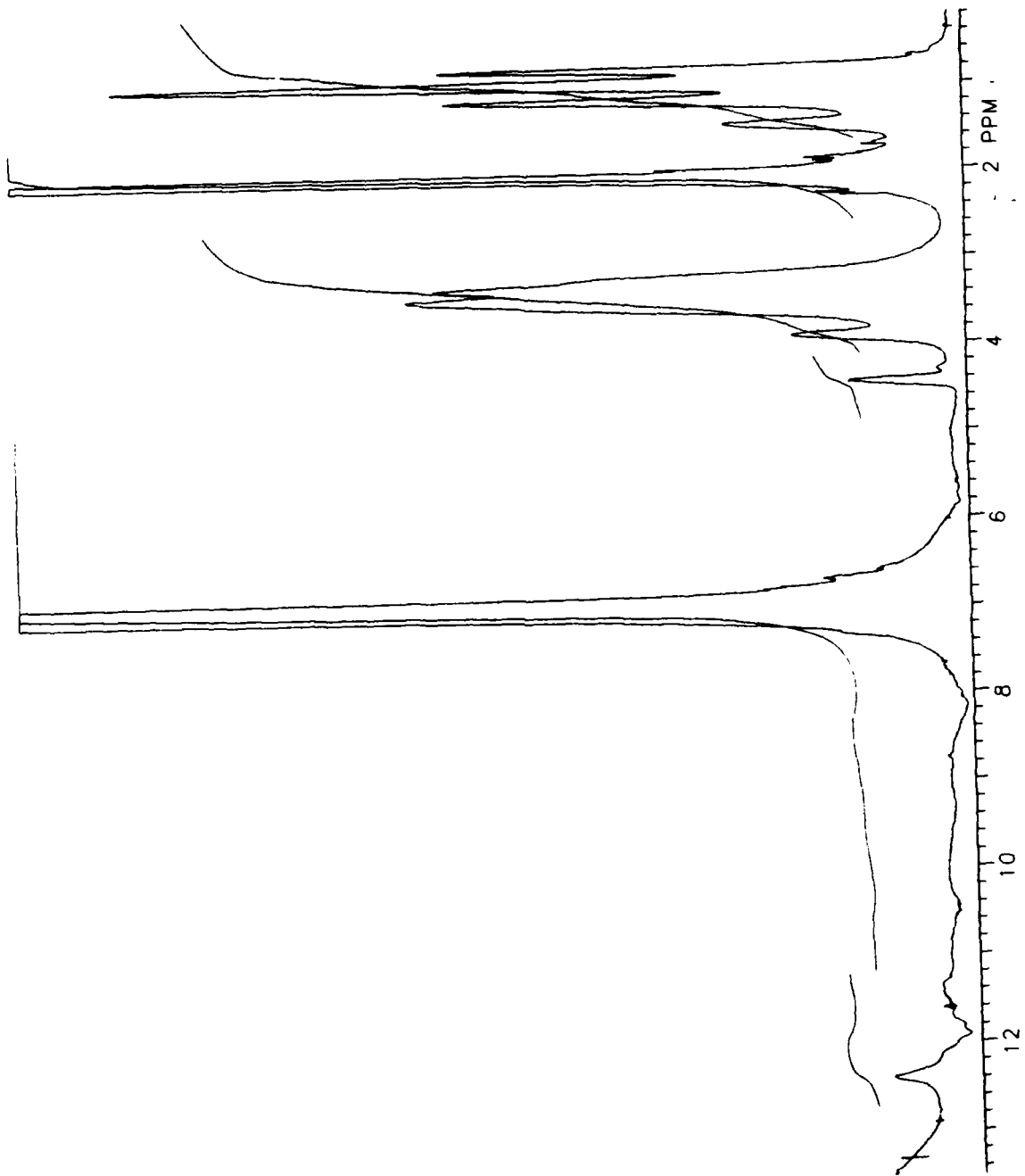


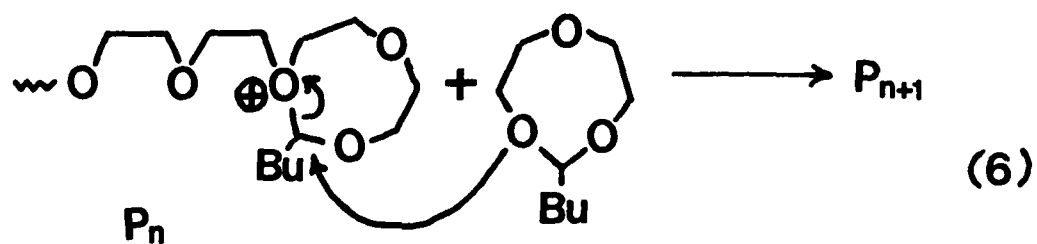
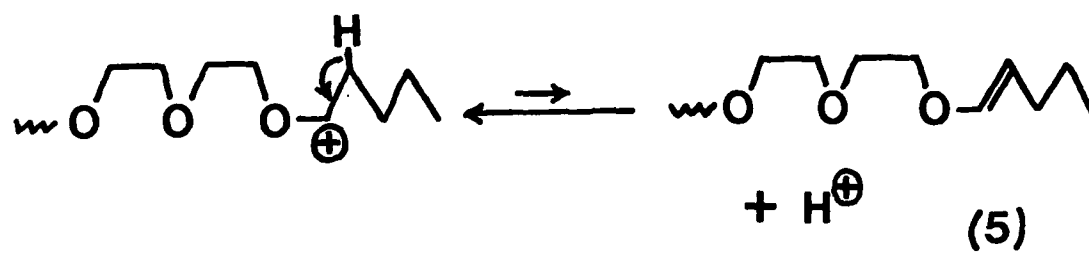
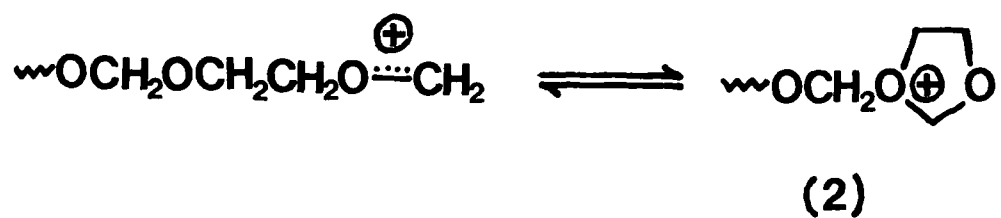
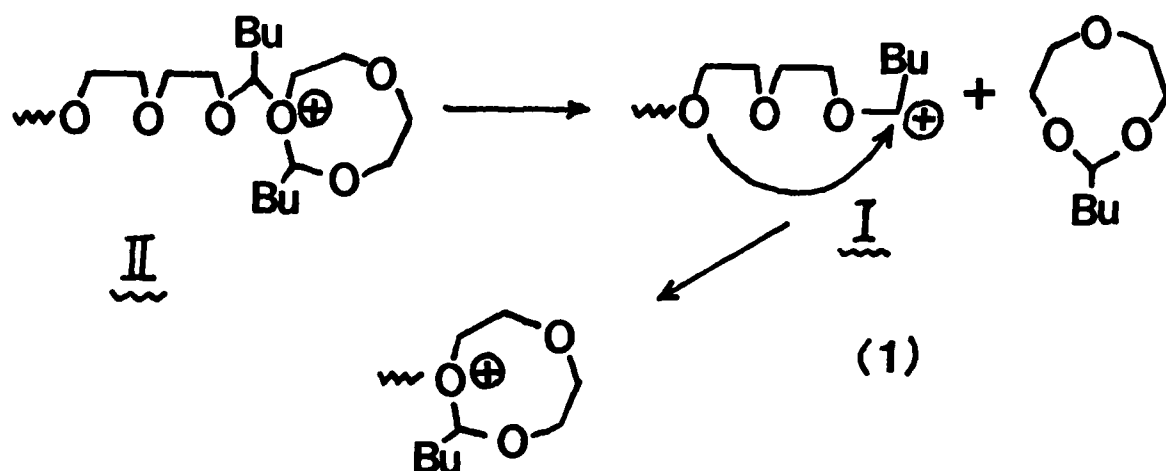












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